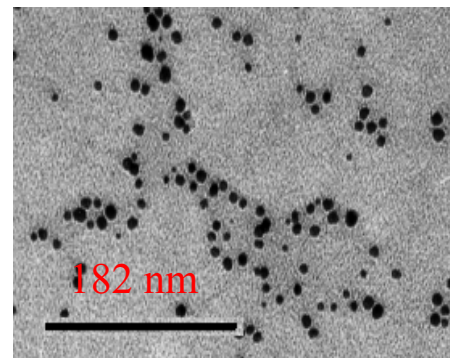


Catalyst Selectivity in Polymer-Protected Nanocatalysts

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It is possible to prepare nanoparticle catalysts by reducing salts of metals such as platinum, palladium, etc. Because the resulting particles are so small, total surface areas are large and catalytic activities can be very high. Such preparations can be carried out in degassed polymer solutions, and the polymer collapsed onto the particles by removal of solvent. The precipitated polymer then protects the nanocatalyst from being deactivated by the environment, specifically water, oxygen, or carbon dioxide. Shelf lives are correspondingly lengthened, and addition of the catalyst simply involves adding a piece of the polymer-protected catalyst to a reaction vessel containing a solvent that will dissolve away most of the polymer carrier.

The fact that very high catalytic efficiencies can be obtained is well documented, but relatively little has been done with regard to *selectivity*. It's now being demonstrated that polymer coatings can be tailored to do this in specific applications. In brief, the polymer coating acts to facilitate or restrict access



A transmission electron microscopy picture of palladium colloids immobilized by polyvinylpyrrolidone (PVPy) with the ratio of polymer to metal being 80/1 (w/w).

of a particular type of substrate to the catalyst surface. In the present example, colloidal palladium nanocatalysts were prepared by *in situ* reductions of palladium chloride. Their selectivities as catalysts were determined by comparing the extents of hydrogenation of carefully chosen pairs of small-molecule olefins. There was found to be high hydrogenation selectivity with regard to cyclic vs non-cyclic olefins, and significant selectivity between two unsaturated cyclic molecules of different sizes. Selectivity could be improved by careful choice of the immobilizing polymer, and by its use at relatively high concentrations. Particularly important extensions of this work would be trying to differentiate between polar and nonpolar substrates by varying the polarity of the

protective polymer, or between negatively-charged and positively-charged substrates by varying the charge of a protective polyelectrolyte.

PVPy/metal ratio	1-Octene	Cyclooctene
40/1	100	75.5
80/1	100	20.0
	Cyclohexene	Cyclooctene
40/1	40.0	29.0
(30 min) 80/1	9.5	8.6

Effect of the ratio of the immobilizing polymer (PVPy) to the metal (Pd) on the selectivity of the hydrogenation of pairs of olefins. (Reaction conditions: 0.2 ml olefins, 0.24 mg Pd, 30 psi hydrogen pressure, 1 hour reaction.)

Most recent reference: "Polymer-protected palladium nanoparticles. Morphologies and catalytic selectivities", Yen T. Vu and James E. Mark, Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, OH 45221-0172, USA. Accepted by **Colloid and Polymer Science**.

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